The High Density Sludge (HDS) Process and Sulphate Control

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ABSTRACT

The high-density sludge (HDS) process has been the standard in the mining industry for treating metal-containing acid rock drainage (ARD), providing low metal levels in the final effluent, and reducing waste sludge volumes compared to other lime based processes. It has been applied for 40 years at mine sites all over the world to meet discharge limits for metals and pH. Recently, various jurisdictions have introduced low discharge limits for sulphate concentrations that are difficult to meet with conventional treatment systems. Also, when treated water is recycled, high sulphate concentrations can cause some undesired downstream impacts. To assist in reducing effluent sulphate concentrations, the recent trend shows that HDS plants have been constructed with considerably higher retentions times in the neutralisation reactors. The reason for this increase in retention time is due primarily to the slow gypsum-precipitation reactions that are the key to minimising sulphate concentrations. These reactions and their effects are explained in detail in this paper. Also discussed are the potential synergies between the HDS process and other processes that treat sulphate more directly. This includes the combination with membrane filtration (reverse osmosis or nanofiltration), with ettringite precipitation, with ion exchange, and even barium precipitation.

Keywords: acid mine drainage sulfate lime treatment

INTRODUCTION

Although many different biological and chemical technologies exist for treatment of acid rock drainage (ARD – or acid mine drainage, AMD), lime neutralisation remains by far the most widely applied treatment method. This is largely due to the high efficiency in removal of dissolved heavy metals combined with the fact that lime costs are low in comparison to alternatives. Lime treatment essentially consists in bringing the pH of the raw water to a point where the metals of concern are insoluble. These metals therefore precipitate to form minuscule particles. A separation of these precipitates is then required to produce a clear effluent which meets regional discharge criteria. The solid/liquid separation forms a sludge which, for a high-density sludge (HDS) process, can contain 10 to 30% solids by weight. This sludge can be further processed to increase the solid content and must be disposed of in an environmentally acceptable manner.

The HDS process has met requirements in the past as the focus for discharge limits has been on toxic metals and acidity. In recent years, there are more and more jurisdictions also including sulphate as a regulated parameter, including Chile and Peru. The specifically applied limits depend on the jurisdiction and often also on the receiver. The limits vary from approximately 2,000 mg/L (as sulphate, SO_4^{2-}) in the high end to as low as 10 mg/L in the receiver.

Lime treatment processes alone cannot meet the low effluent sulphate limits and even the higher limits in some cases. But there are modifications that can be brought to the HDS process which help minimise the final sulphate concentration either as a stand-alone treatment or in conjunction with other sulphate treatment systems. In this paper, the lime treatment of ARD is summarised and the associated minimisation of sulphate concentration is also explained.

THE BASIC CHEMISTRY OF LIME TREATMENT

The principle of lime neutralisation of ARD lies in the insolubility of heavy metals in alkaline conditions. By controlling pH to a typical setpoint of 9.5, metals such as iron (Fe), zinc (Zn), and copper (Cu) are precipitated (see Figure 1). Other metals such as nickel (Ni) and cadmium (Cd) require a higher pH, in the range of 10.5 to 11 to effectively precipitate the hydroxides. The precipitates can be formed individually as minuscule particles smaller than a single micron (1 μm). In a high-density sludge process, the precipitates are formed onto existing particles recycled within the process. This creates larger and denser particles that settle and compress better than the precipitates created with direct lime addition. This essentially defines the greatest difference between the HDS process and other lime treatment processes: the method of precipitating and separating the solids and the sludge that is formed.

It is important to note that the precipitation reactions and resulting precipitates are shown and discussed as per theory. In reality, almost all of the precipitates are amorphous mixtures of many metals, hydroxides, sulphates, and other ions present in solution, with several of the ions adsorbed and not truly precipitated in the presented form. The only actual crystals often identified in fresh sludge are calcite and gypsum. Aged sludges can contain other crystalline forms (Zinck, 2005).
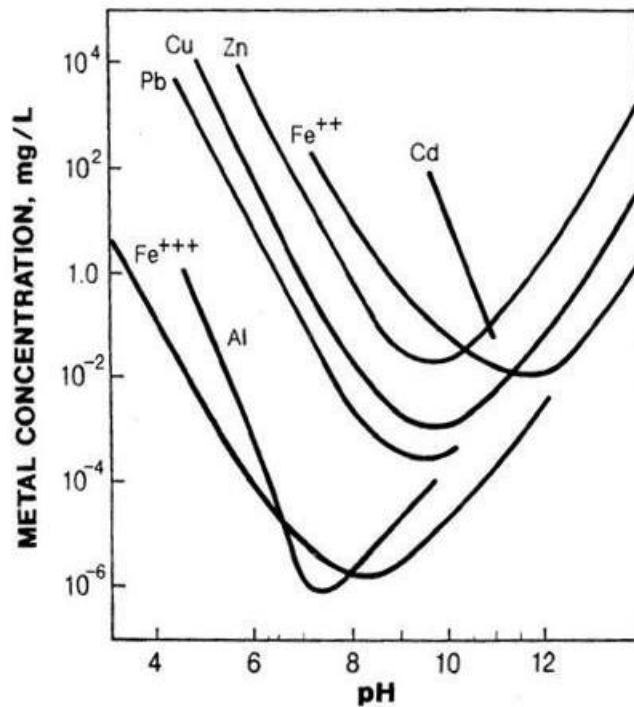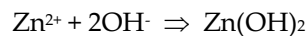
Figure 1 Metal Hydrolysis (from Aubé and Zinck, 2003)

Lime dissolution is the first step of the neutralisation process. For large treatment systems, quicklime is used. This lime must first be hydrated (slaked) and is normally fed to the process as a slurry. When fed to the process, the hydrated lime then dissolves to increase pH. The two following equations illustrate these reactions:

$$CaO + H_2O \Rightarrow Ca(OH)_2$$

$$Ca(OH)_2 \Rightarrow Ca^{2+} + 2OH^-$$
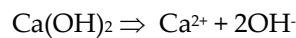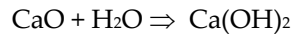
The increased pH then provides hydroxide ions which combine with the dissolved metals to produce precipitates. The following equations show the precipitation reactions with different metals:
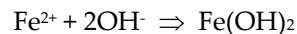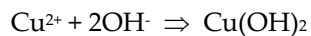
$$Al^{3+} + 3OH^- \Rightarrow Al(OH)_3$$

$$Co^{2+} + 2OH^- \Rightarrow Co(OH)_2$$

$$Cu^{2+} + 2OH^- \Rightarrow Cu(OH)_2$$

$$Fe^{2+} + 2OH^- \Rightarrow Fe(OH)_2$$

$$Fe^{3+} + 3OH^- \Rightarrow Fe(OH)_3$$

$$Ni^{2+} + 2OH^- \Rightarrow Ni(OH)_2$$

$$Pb^{2+} + 2OH^- \Rightarrow Pb(OH)_2$$

$$Zn^{2+} + 2OH^- \Rightarrow Zn(OH)_2$$
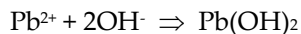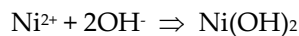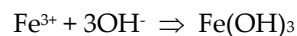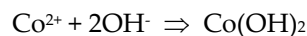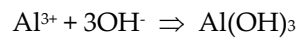
The resulting water quality contains very low heavy metal concentrations due to this hydroxide precipitation. Proportional to the precipitation of these metals is the solubilisation of calcium from the lime. Effectively, for the dissolved ionic balance, Ca replaces the heavy metals in solution. This leads to the precipitation of gypsum as per the following equation:

$$Ca^{2+} + SO_4^{2-} \Rightarrow CaSO_4{\cdot}2H_2O$$
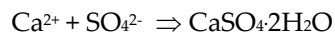
What differentiates gypsum from the metal hydroxides is that the metals precipitate very rapidly while gypsum precipitates slowly. Most lime treatment plant effluents are super-saturated for gypsum upon discharge. The reasons for this and the effects that are caused by this slow precipitation are discussed in greater detail in the following sections.

THE SULPHATE PROBLEM STATEMENT

In most sulphide mines, some precious metal mines, and some coal mines, the waste rock and tailings contain iron and other metal sulphides which oxidise to form AMD containing sulphuric acid and dissolved metals. This AMD problem is well documented in numerous other publications. Historically, AMD was either treated to remove toxicity and released to the environment or treated for recycle to the process (concentrator) with high sulphate concentrations.

Sulphate control has become a greater concern in recent years because it has been added as a regulated parameter in many jurisdictions. Sulphate concentrations can also present problems when the treated water is recycled. The gypsum formation discussed above also results in significant scaling issues, both within treatment plants and downstream. Within a conventional lime treatment plant there can be significant scaling on all surfaces, particularly in reactors where the lime is added when there is no sludge recirculation. Even with sludge recirculation, it is the clarifier overflow weir, effluent piping, flume, turbidimeters, and pH probes that sustain the greatest amount of scaling.

For some sites where the treated water is recycled as process water, the scaling caused by gypsum formation can be a critical cost issue. In one European underground mine, the recycled water used in the mine for cooling the drills (jumbos) via oil-water intercoolers results in significant scaling of these items and high maintenance costs. A gypsum-saturated solution also cannot be used as gland water for pumps due to the significant maintenance requirements. Scaling in process water piping and valves can also create issues with control and even safety concerns.

There are two main reasons for the scaling issues: 1) the gypsum precipitation reaction is slow and 2) gypsum is a crystal that preferentially forms on existing gypsum crystals.

While hydroxide reactions that cause the precipitation of metals are almost instantaneous, gypsum formation can take days to reach equilibrium. The comparatively slow precipitation is primarily a function of kinetics but can also be related to the solubility product constant (Ksp). The heavy metal hydroxide precipitates listed above have solubility constants in the order of 10^{-15} to 10^{-30}. Gypsum has a solubility product constant of 2.4 $x10^{-5}$ which is at least 10 orders of magnitude higher than that of the hydroxides. Kinetics can also be linked to size of the ions involved in the formation of the solid. In the case of the metal precipitates, all are related to the hydroxide ion, which is extremely mobile in an aqueous solution. For gypsum, the calcium mobility can be compared to that of the heavy metals, while the sulphate molecule, which is a much larger molecule than that of the hydroxide, is considerably less mobile.

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Another important aspect of gypsum precipitation is that it occurs considerably more readily on existing gypsum crystals than by nucleation. Metal hydroxide particles readily nucleate in a solution that contains no solids, given the right pH conditions. Gypsum does not tend to nucleate but rather to form on a solid surface, preferably on existing gypsum. In clear water, without the presence of gypsum particles or other solids in suspension, the only existing surfaces are from the equipment and walls. An initial coating of gypsum forms on equipment surfaces, then these surfaces act as a seeding location for continued precipitation. This distinctiveness for gypsum explains why scaling on equipment surfaces occurs more readily in clear water, following solid-liquid separation.

THE HDS PROCESS

The high density sludge (HDS) process is the standard in the AMD treatment industry today (**Figure 2**). Instead of contacting lime directly to the AMD, this process first contacts recycled sludge with the lime slurry for neutralisation. To do this, the sludge from the clarifier bottom is pumped to a "Lime/Sludge Mix Tank" where sufficient lime to neutralise the AMD to the desired pH setpoint is also fed. This forces contact between the solids and promotes coagulation of lime particles onto the recycled precipitates. This mixture then overflows to the Lime Reactor (LR) where pH is controlled and the precipitation reactions are completed. Aeration is often added to this reactor to oxidise ferrous iron to ferric and form the more stable ferric hydroxide.
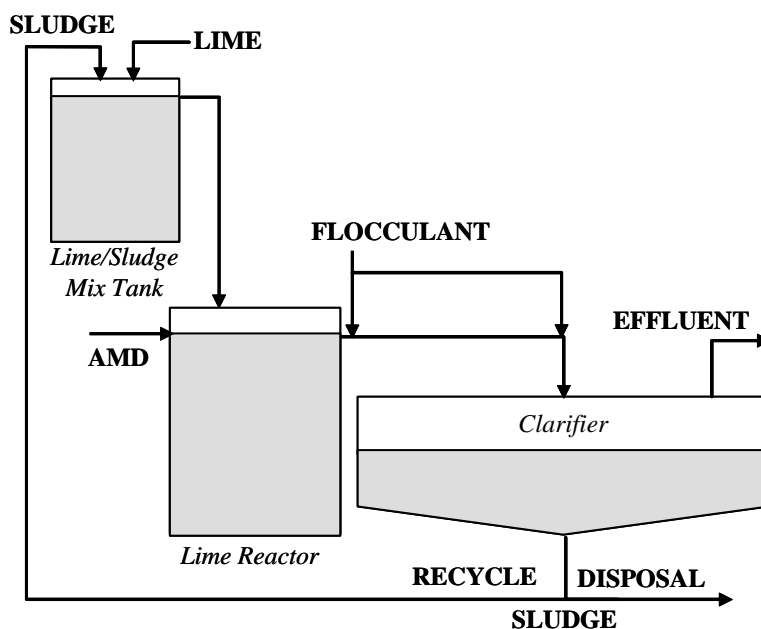

Figure 2 Simplified Representation of HDS Process

The slurry is then contacted to a flocculant solution either via a Flocculation Tank or by providing turbulence in the conduit leading from the Lime Reactor to the clarifier. A trough with baffles may be sufficient to ensure proper contact with the small particles. The flocculant serves to agglomerate

all precipitates and promote efficient settling in the clarifier. The clarifier overflow can either be discharged or recycled as process water as-is or polished prior to the next step. A simplified representation of the HDS process is shown in Figure 2.

The key to this process lies in the mixing of lime and sludge prior to neutralisation. The fact that the calcium hydroxide and recycled particles are combined causes the precipitation reactions to occur mostly on the surface of existing particles, thereby increasing their size and density. The precipitates from this process are therefore different from those where this lime/sludge mixture does not occur.

The HDS process presents significant advantages in operating costs over conventional lime addition, due the increased sludge density, decreased lime consumption, improved metal removal, and better solid/liquid separation (Aubé and Zinck, 1999). The higher sludge density means less waste is produced but also that more water is treated and released (or recycled).

Sulphate in the HDS Process

As discussed previously, a critical part of the HDS process is the Lime/Sludge Mix Tank, where recycled sludge is contacted with a concentrated lime slurry. The lime addition rate here is controlled by the desired setpoint in the Lime Reactor. Typically, the pH in this reactor is higher than 11 and can be as high as 12.5. As this high pH is due to lime dissolution, the calcium concentrations are very high. This promotes gypsum precipitation in this location and provides a high concentration of gypsum needles for the Lime Reactor. This is shown in Figure 3 in a scanning electron micrograph (SEM) of a freeze-dried slurry collected from an industrial Lime/Sludge Mix Tank. The needles in Figure 3 are gypsum crystals.
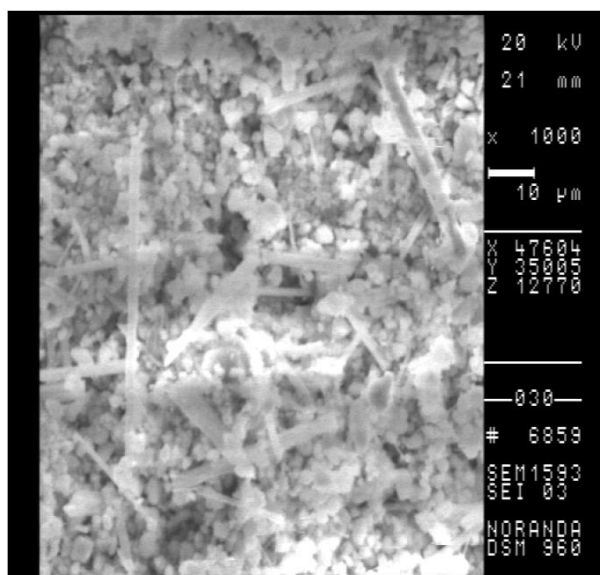

Figure 3 SEM Photograph of a Lime/Sludge Mixture

Modifications to the HDS Process for Improved Sulphate Removal

The major modification incorporated into the HDS process for improved sulphate control is to increase retention time in the reactors. This can be done by using multiple reactors in series. Table 1

shows a summary of HDS treatment plants built late in the past century (sites A to D), in comparison with more recent plants (sites 1 to 3) that were designed with a focus on sulphate concentrations. It is clear that the trend applied by process engineers in recent years is to add more reactors and greater retention time. In case of scaling issues, the reactors are often designed to be by-passed. This is true of the Geco plant (Site 1), for example, where either of the first two reactors can be by-passed. The other two examples can have any of the neutralisation reactors by-passed.

Table 1 Example HDS Plant Reactor Retention Times

Site	Start-up (year)	Treatment Flowrate (L/min)	Number of Reactors	Total Design Retention Time (minutes)
A	1984	3 000	2	40
B	1993	60 000	1	40
C	1993	10 000	1	40
D	1997	20 000	1	45
1	2005	15 500	3	150
2	2011	5 833	2	120
3	2014	30 000	3	120

A high sludge recycle rate also increases the concentration of gypsum crystals in the neutralising reactors to help promote additional gypsum precipitation. But the recycle rate can be limited by the efficiency of flocculant contact and solid/liquid separation; too high a recycle will lead to a high solid content in the slurry and can make flocculation difficult.

By applying these principles of increased retention time in the reactors where a continuous contact with existing gypsum crystals is provided by high sludge recycle, the resulting sulphate concentrations are lower as the slurry reaches the clarifier. There are limitations in the removal of sulphate in an HDS plant related not only to the kinetics of gypsum precipitation but also to the chemistry of the raw water. The gypsum precipitation occurs in large part due to Ca replacing heavy metals as the cation associated to sulphate. Some cations do not precipitate in HDS treatment, particularly alkali metals such as sodium (Na) and potassium (K). Magnesium may also remain in solution if the pH control point is less than 10. Sulphate concentrations will be higher in HDS-treated effluent if the AMD contains significant concentrations of these light metals. The final sulphate concentration therefore varies from site to site despite applying the same process, as the raw water chemistry varies significantly.

Some scaling is still likely to occur in HDS treatment plants, particularly in the effluent systems and reactor aeration systems. The more recent designs allow for maintenance to remove scaling where it may become problematic. Launders and flow-measuring devices are open or with removable covers for access to remove accumulated scaling. For the aeration systems in the reactors, the ability to by-pass a reactor can allow for maintenance while continuing treatment. Large man-doors are included in the design of the reactors for rapid access. Clarifiers can be equipped with larger access to facilitate using a small tractor (such as a Bobcat) to remove the accumulated scale. At mine sites

with high sulphate concentrations, it may be necessary to shut down on an annual basis for a week or two specifically for this clarifier cleaning.

Combination of HDS with Other Treatment Methods

In order to meet some effluent regulations for sulphate, HDS treatment cannot be applied alone. In these cases, other technologies can be used to treat for sulphate specifically. Four of these potential sulphate treatment technologies are discussed below, including membrane separation, ion exchange, ettringite precipitation, and barium precipitation.

The limitations inherent in the sulphate treatment technologies discussed below are the main reasons for their reduced applicability seen at the full scale. The following sections describe the opportunities to optimise these sulphate technologies through combination with the HDS process.

Membranes

The leading method of control for sulphate in the mining industry at this time is by membrane separation. These reverse osmosis (RO) or nano-filtration (NF) systems can produce a permeate capable of meeting any sulphate limit. The greatest disadvantage of this process is the formation of a concentrate (or brine) stream that often represents more than 30% of the initial raw water volume. The HDS process can be used to treat this high-sulphate concentrate to greatly reduce the final waste volume. Treatment of the brine with HDS can provide the required bleed of sulphate in the form of gypsum in the waste sludge, while the clarifier overflow can either be returned for re-treatment in the RO or mixed with the RO permeate depending on the target sulphate level in the final effluent.

The greatest challenge with membrane treatment for sulphate in the mining industry is the formation of gypsum in the membranes themselves, due to the super-concentration of the brine as it advances across the membrane. This gypsum precipitate is commonly due to the fact that the ARD contains sulfuric acid that has been neutralised with lime, thereby feeding a gypsum super-saturated solution to the membrane from the start. This scaling issue significantly reduces the service life of the membranes. Gypsum scaling can be reduced by decreasing recovery rates, backwashing, increasing tangential flow, and/or adding an anti-scalant. Each of these options increases treatment costs due to decreased discharge fractions (more recycled brine), increased pressures (higher energy costs), and/or high reagent costs.

Recent advances in membrane materials have resulted in NF membranes that can tolerate very low pH. In some applications, with a low pH stream containing high levels of metals and sulphate, it is possible to treat this stream with NF membranes with only particle filtration as a pre-treatment. At this low pH, prior to lime addition, the solubility level of gypsum is higher and the available calcium is lower, resulting in a decreased scaling potential in the NF membranes. This results in considerably higher recovery rates, with concentrate streams of less than 25% of the raw ARD feed. This can significantly reduce costs as the membranes last longer and the use of anti-scalants is reduced or even eliminated.

The NF permeate can then be combined with the balance of the AMD for further treatment in an HDS plant, but now the issues with gypsum scaling are reduced. The NF concentrate can be treated in an HDS process to further reduce the waste stream. If RO is required as a final treatment, the NF and RO concentrate streams can be combined and treated in the same HDS plant.

Essentially, membrane treatment alone would result in a significant waste stream and still require pH adjustment. To reduce waste, to present an outlet for sulphate (as gypsum), and increase overall water recovery in an economic manner, HDS is best used in conjunction with membrane treatment.

Ion Exchange

Another process offered by suppliers for sulphate treatment is ion exchange . In this process, two stages are applied with very specific ion exchange resins. One example of this process is the GYP-SIX process (Robertson and Rohrs, 1995). The cationic resin is specific for calcium and the anionic is specific for sulphate. The regeneration is performed with sulphuric acid on the cationic side and lime-saturated solution on the anionic side. The process produces gypsum as a by-product (or most likely as a waste). The proposed IX processes do not treat all contaminants to make the water compliant for discharge or recycle to a concentrator. One option is the application of the HDS process upstream of the IX process, and by minimising the concentrations of sulphate, it will be possible to reduce the overall costs of water treatment.

Ettringite

There are many suppliers presently proposing the ettringite process for sulphate control. This process has been proven to bring sulphate concentrations low but has the disadvantage of high costs due to the need for an aluminium (Al) reagent and the production of large volumes of low-density sludge. This is shown in the formula below.

$$6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_3 + 32\ H_2O \Rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O + 6H^+$$
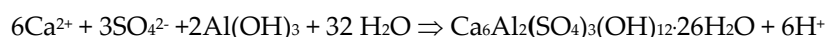
In some cases, such as the CESR process (INAP, 2003), there is a metal precipitation step prior to ettringite formation. If the HDS process with an extended retention time in the neutralisation reactors were to be applied in this initial metal precipitation step, the initial sulphate concentrations for the ettringite step will be reduced. This would serve to decrease the consumption of the expensive Al reagent in the ettringite step. This will also significantly reduce the volume of sludge produced as the HDS process can form a sludge containing more than 20% solids with a significant sulphate (gypsum) content. The ettringite sludge is viscous and can contain less than 2% solids.
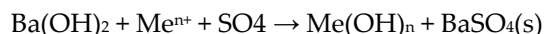
Barium Precipitation

Another well-known process for treatment of sulphate is precipitation using barium (Ba). It may be possible to integrate Ba into existing HDS treatment systems thereby reducing unnecessary and expensive capital investments. New systems could also incorporate Ba after lime addition. As a specific process for sulphate precipitation, Ba is not currently used in the full scale. This is due to high cost of the raw reagent, as Ba is not readily available in the quantities that would be required.

At a high pH, the addition of barium carbonate can be used to decrease sulphate concentrations via the following reaction:

$$Ca^{2+} + SO_4^{2-} + BaCO_3(s) \rightarrow BaSO_4(s) + CaCO_3(s)$$
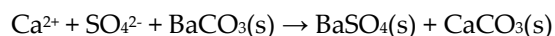
It is also possible to use barium hydroxide directly, where the main process reaction would be the following:

$$Ba(OH)_2 + Me^{n+} + SO4 \rightarrow Me(OH)_n + BaSO_4(s)$$

Me represents the metal components of the effluent stream, typically iron, zinc, nickel, copper, cadmium, or cobalt. Barium chloride can also be used for sulphate precipitation but this process

will put into solution as much chloride as there is sulphate removed, thus exchanging one problem with another.

Prior treatment with the HDS process can help reduce the sulphate concentration and thus the operating costs of the sulphate treatment process as it decreases the consumption of barium.

CONCLUSION

Recent trends to improve the sulphate treatment in HDS plants involve longer retention time in neutralisation reactors as a primary modification. The process requires an optimised control of solids recirculation to provide sufficient gypsum seeding from sludge without negatively impacting the solid/liquid separation. The ability to access the equipment and by-pass reactors is also important for maintenance when treating high-sulphate waters.

The HDS process can be successfully combined with membrane filtration either before or after to control the effluent quality as required and minimise liquid waste from the concentrate. The HDS process is also uniquely suited to work with ettringite, barium, or ion exchange processes to reduce total treatment costs and waste management.

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